

INVESTIGATIONS FOR DENDRITE SUPPRESSION IN LITHIUM AND SODIUM METAL BATTERIES

A thesis presented for the award of the degree of

Doctor of Philosophy

from

University of Technology Sydney

By

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DEDICATION

This thesis is dedicated to my family.

CERTIFICATE OF ORIGINAL AUTHORSHIP

I, Kang Yan, declare that this thesis, is submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the Faculty of Science at the University of Technology Sydney.

This thesis is wholly my own work unless otherwise reference or acknowledgement. In addition, I certify that all information sources and literature used are indicated in the thesis.

This document has not been submitted for qualifications at any other academic institution.

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Kang Yan

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STATEMENT OF FORMAT

This is the statement indicating that three published work are included in this thesis. Three original published work are referred to chapter 3, chapter 4 and chapter 5. The related publications in this thesis are listed as follows:

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RESEARCH PUBLICATIONS

1. **Kang Yan**, Shuoqing Zhao, Jinqiang Zhang, Javad Safaei, Xingxing Yu, Tianyi Wang, Shijian Wang, Bing Sun, Guoxiu Wang, Dendrite-Free Sodium Metal Batteries Enabled by the Release of Contact Strain on Flexible and Sodiophilic Matrix, **Nano Letters**. 2020, DOI: 10.1021/acs.nanolett.0c02215.
2. **Kang Yan**, Jiangyan Wang, Shuoqing Zhao, Dong Zhou, Bing Sun, Yi Cui, Guoxiu Wang, Temperature-Dependent Nucleation and Growth of Dendrite-Free Lithium Metal Anodes, **Angewandte Chemie International Edition**. 2019, 58 (33), 11364-11368.
3. **Kang Yan**, Bing Sun, Paul Munroe, Guoxiu Wang, Three-Dimensional Pie-Like Current Collectors for Dendrite-Free Lithium Metal Anodes, **Energy Storage Materials**. 2018, 11, 127-133.
4. Shuoqing Zhao, Liubing Dong, Bing Sun, **Kang Yan**, Jinqiang Zhang, Shuwei Wan, Fengrong He, Paul Munroe, Peter HL Notten, Guoxiu Wang, $K_2Ti_2O_5@C$ Microspheres with Enhanced K^+ Intercalation Pseudocapacitance Ensuring Fast Potassium Storage and Long-Term Cycling Stability, **Small**. 2020, 16 (4), 1906131.
5. Jinqiang Zhang, Yufei Zhao, Chen Chen, Yu-Cheng Huang, Chung-Li Dong, Chih-Jung Chen, Ru-Shi Liu, Chengyin Wang, **Kang Yan**, Yadong Li, Guoxiu Wang, Tuning the Coordination Environment in Single-Atom Catalysts to Achieve Highly Efficient Oxygen Reduction Reactions, **Journal of the American Chemical Society**. 2019, 141 (51), 20118-20126.
6. Xiao Tang, Dong Zhou, Peng Li, Xin Guo, Bing Sun, Hao Liu, **Kang Yan**, Yury Gogotsi, Guoxiu Wang, MXene-Based Dendrite-Free Potassium Metal Batteries, **Advanced Materials**. 2020, 32 (4), 1906739.
7. Bing Sun, Pan Xiong, Urmimala Maitra, Daniel Langsdorf, **Kang Yan**, Chengyin Wang, Jürgen Janek, Daniel Schröder, Guoxiu Wang, Design Strategies to Enable the Efficient Use of Sodium Metal Anodes in High-Energy Batteries, **Advanced Materials**. 2019, 32 (18), 1903891.
8. Shuoqing Zhao, **Kang Yan**, Paul Munroe, Bing Sun, Guoxiu Wang, Construction of Hierarchical $K_{1.39}Mn_3O_6$ Spheres via AlF_3 Coating for High-Performance Potassium-Ion Batteries, **Advanced Energy Materials**. 2019, 9 (10), 1803757.

9. Jinqiang Zhang, Bing Sun, Yufei Zhao, Anastasia Tkacheva, Zhenjie Liu, **Kang Yan**, Xin Guo, Andrew M McDonagh, Devaraj Shanmukaraj, Chengyin Wang, Teofilo Rojo, Michel Armand, Zhangquan Peng, Guoxiu Wang, A Versatile Functionalized Ionic Liquid to Boost the Solution-Mediated Performances of Lithium-Oxygen Batteries, **Nature communications**. 2019, 10 (1), 1-10.
10. Shuoqing Zhao, Bing Sun, **Kang Yan**, Jinqiang Zhang, Chengyin Wang, Guoxiu Wang, Aegis of Lithium-Rich Cathode Materials via Heterostructured LiAlF₄ Coating for High-Performance Lithium-Ion Batteries, **ACS applied materials & interfaces**. 2018, 10 (39), 33260-33268.
11. Wu Yang, Wang Yang, Bing Sun, Shuanlong Di, **Kang Yan**, Guoxiu Wang, Guangjie Shao, Mixed Lithium Oxynitride/Oxysulfide as An Interphase Protective Layer to Stabilize Lithium Anodes for High-Performance Lithium-Sulfur Batteries, **ACS applied materials & interfaces**. 2018, 10 (46), 39695-39704.
12. Shuoqing Zhao, **Kang Yan**, Jinqiang Zhang, Bing Sun and Guoxiu Wang, Reviving Reaction Mechanism of Layered Lithium-Rich Cathode Materials for High-Energy Lithium-Ion Battery, **Angewandte Chemie International Edition**. 2020, DOI: 10.1002/anie.202000262.
13. Xingxing Yu, Zi-You Yu, Xiao-Long Zhang, Peng Li, Bing Sun, Xiaochun Gao, **Kang Yan**, Hao Liu, Yu Duan, Min-Rui Gao, Guoxiu Wang, Shu-Hong Yu, Highly Disordered Cobalt Oxide Nanostructure Induced by Sulfur Incorporation for Efficient Overall Water Splitting, **Nano Energy**. 2020, 71, 104652.
14. Fan Zhang, Xin Guo, Pan Xiong, Jinqiang Zhang, Jianjun Song, **Kang Yan**, Xiaochun Gao, Hao Liu, Guoxiu Wang, Interface Engineering of MXene Composite Separator for High-Performance Li-Se and Na-Se Batteries, **Advanced Energy Materials**. 2020, 10, 2000446.

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ABSTRACT

Lithium (Li) metal possesses very high specific capacity and low electrochemical potential, which shows great advantages to be used in next generation rechargeable Li metal batteries (LMBs). However, poor cyclability of Li metal anodes caused by inhomogeneous and uncontrolled Li deposition hinders the practical applications of rechargeable LMBs. Here, in order to effectively suppress Li dendrite growth without degrading the specific capacity, a three-dimensional (3D) pie-like current collector was prepared based on copper nanowires (CuNWs) and graphene (GE). The interior space of CuNWs framework efficiently accommodate Li deposition. Meanwhile, the GE layer wrapped outside CuNWs functions as flexible protective layer that could protect extra Li deposition. The CuNWs@GE current collectors demonstrated several merits to achieve better Li metal anodes with significantly improved Coulombic efficiency and cyclability for rechargeable LMBs.

It is essential to develop a facile and effective method to enhance the electrochemical performance of Li metal anodes for building high-energy-density LMBs. Herein, we explored the temperature-dependent Li nucleation and growth behavior and constructed a dendrite-free Li metal anode by elevating temperature from room temperature (20 °C) to 60 °C. A series of *ex situ* and *in situ* microscopy investigations demonstrate that increasing Li deposition temperature results in large nuclei size, low nucleation density, and compact growth of Li metal. We reveal that enhanced lithiophilicity and increased Li-ion diffusion coefficient in aprotic electrolytes at high temperature are essential factors contributing to the dendrite-free Li growth. As anodes in both half-cell and full-cell, the compact deposited Li

with minimized specific surface area delivered high Coulombic efficiencies and long cycling stability at 60 °C.

The formation of sodium (Na) dendrites during cycling has impeded the practical application of Na metal anodes. Herein, we developed a flexible graphene-based matrix, *e.g.*, porous reduced graphene oxide (PRGO) film, to support dendrite-free Na nucleation and plating, contributing to high-performance Na metal batteries. The PRGO film possessed outstanding merits of sodiophilicity and flexibility. The sodiophilic PRGO film enabled uniform Na nucleation. Furthermore, the flexible PRGO film alleviated the texture deformation of electrodeposited Na, leading to a compact and dendrite-free Na deposition layer. The well-maintained Na metal anodes on PRGO films exhibited superior cyclability, high Coulombic efficiency, and improved energy density in both half-cell and full-cell testing. This work illustrates the great significance of mechanical properties of the supporting matrix for the Na electroplating, which provides a new strategy to develop high-performance dendrite-free Na metal batteries.